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FACILITY FORM 602	N66-18447	
	(ACCESSION NUMBER)	(THRU)
	22 (PAGES)	1 (CODE)
	(NASA CR OR TMX OR AD NUMBER)	B3 (CATEGORY)

Translation of "Raschet termodinamicheskikh svoystv kaliya pri  
temperaturakh do 1300°C i davleniyakh do 25 kg/sm<sup>2</sup>".  
Teploenergetika, Vol.9, No.10, pp.65-72, 1962.

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 1.00Microfiche (MF) .50

ff 653 July 65

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON JANUARY 1966

CALCULATION OF THERMODYNAMIC PROPERTIES OF POTASSIUM AT TEMPERATURES OF UP TO 1300°C AND PRESSURES OF UP TO 25 kg/cm<sup>2</sup> \*/65

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A method of calculating the thermodynamic properties of the superheated and wet vapors of a dissociating ideal gas ( $X_2 \rightleftharpoons 2X$ ) is further elaborated. Tables of the thermodynamic properties of potassium vapors at up to 1300°C and ~ 25 kg/cm<sup>2</sup> are presented, permitting ready calculation of derivatives for the theory of associating gases, at  $\mu = \text{const}$ , forming the basis for computation of dissociating gases. Author

At present, gases subject to the dissociation reaction  $X_2 \rightleftharpoons 2X$  at elevated temperatures are of considerable interest.

For such gases, considered as an equilibrium mixture of reacting ideal mon-atomic and diatomic components, we compiled in an explicit form a Table of first-order partial derivatives for the thermodynamic parameters: pressure  $p$ , temperature  $T$ , degree of dissociation  $\alpha$ , as well as for the unit quantities volume  $v$ , entropy  $s$ , enthalpy  $i$ , intrinsic energy  $u$  (Table 1).

The method of constructing Tables of this kind, with derivatives expressed in a general form, is described elsewhere [for example (Bibl.1)]. To convert the partial derivatives to their explicit form, we used the equation of state of an ideal dissociating gas (Bibl.2, 3):

$$v = \frac{RT(1 + \alpha)}{\mu_1 p}, \quad (1)$$

\* Numbers in the margin indicate pagination in the original foreign text.

where

$R = 847.83 \text{ kg-m/kmol/}^\circ\text{K}$  is the universal gas constant;

$\alpha = \left(1 + \frac{4p}{K_e}\right)^{-1/2}$  is the degree of dissociation of the reaction

$X_2 \rightleftharpoons 2X$ , the ratio of the reacted number of moles  $X_2$  to the original number;

$K_e$  is the equilibrium constant, determined by the conventional method (Bibl.3, 4) in accordance with the difference in standard isobar-isotherm potentials of the components; for a mixture of ideal gases  $K_e$  is a function of temperature alone, in accordance with the equation

$$\left(\frac{\partial \ln K_e}{\partial T}\right)_p = \frac{\Delta I^\circ}{RT^2}.$$

where

$\Delta I^\circ = D_0^\circ + 2(I^\circ - I_0^\circ)_1 - (I^\circ - I_0^\circ)_2$  is the thermal effect of the reaction per kilomole of  $X_2$ ;

$D_0^\circ$  is the heat of dissociation per mole of  $X_2$  for  $T = 0^\circ\text{K}$ ;

$I^\circ - I_0^\circ$  is the standard enthalpy per mole of component, computed from the state of  $I_0^\circ$  at  $T = 0^\circ\text{K}$ ;

$$1/A = 426.94 \text{ kg-m/kcal.}$$

The subscripts 1 and 2 refer to the components  $X_1$  and  $X_2$ , respectively; the superscript 0 denotes the ideal-gas state at  $p = 1 \text{ atm (phys)}$ .

The derivatives are more conveniently determined by means of parameters other than molar, since the molecular weight of the reacting mixture is a variable and the thermodynamic relations usually apply to systems with a constant mass.

TABLE 1

FIRST-ORDER PARTIAL DERIVATIVES OF DISSOCIATING IDEAL GAS  $|X_2 \rightleftharpoons 2X|$ 

$$pv = \frac{RT(1+\alpha)}{\mu_2}; \quad \xi = \frac{\alpha(1-\alpha)}{2}; \quad h = \frac{\Delta i^0}{ART}$$

	$p = \text{const}$	$T = \text{const}$	$v = \text{const}$	$\alpha = \text{const}$	$i = \text{const}$	$\mu = \text{const}$	$\mu = \text{const}$ $\mu = \text{const}$
$\partial p$	—	—1	$-\frac{1+h\cdot\xi}{T} v$	$-\frac{c_p}{T}$	$-c_p$	$\frac{Apv(1+h\xi)}{T} - c_p$	$-\frac{h\cdot\xi(1+\alpha)}{T}$
$\partial T$	1	—	$-(1+\xi)\frac{v}{p}$	$-\frac{A(1+h\cdot\xi)v}{T}$	$-A\cdot h\cdot\xi\cdot v$	$A\xi(1-h)v$	$-\frac{\xi(1+\alpha)}{p}$
$\partial v$	$\frac{1+h\cdot\xi}{T} v$	$(1+\xi)\frac{v}{p}$	—	$\frac{c_p(1+\xi)v}{pT}$	$-\left[\frac{c_p(1+\xi)}{p} + \frac{A(1+h\cdot\xi)v}{T}\right] v$	$\frac{c_p(1+\xi)v}{p}$	$\frac{\xi(1+\alpha)(1-h)\cdot v}{pT}$
$\partial i$	$\frac{c_p}{T}$	$\frac{A(1+h\xi)v}{T}$	$-\frac{c_p(1+\xi)v}{p\cdot T}$	—	$-\frac{Ac_p v}{T}$	$\frac{Ac_p(1+\xi)v}{T}$	$-\frac{\xi(1+\alpha)}{\mu_2 p T} [2ac^0_{p1} + (1-\alpha)c^0_{p2} - AR(1+\alpha)h]$
$\partial \mu$	$c_p$	$A\cdot h\cdot\xi\cdot v$	$\left[\frac{c_p(1+\xi)}{p} + \frac{A(1+h\cdot\xi)v}{T}\right] v$	$\frac{Ac_p v}{T}$	—	$Ac_p(1+\xi)v - Av\left[c_p - \frac{A(1+h\cdot\xi)pv}{T}\right]$	$-\frac{\xi(1+\alpha)}{p\mu_2} \times [2ac^0_{p1} + (1-\alpha)c^0_{p2}]$
$\partial \alpha$	$c_p - \frac{Apv(1+h\cdot\xi)}{T}$	$A\cdot\xi(h-1)v$	$-\frac{c_p(1+\xi)v}{p}$	$-\frac{Ac_p(1+\xi)v}{T}$	$Av\left[c_p - \frac{A(1+h\cdot\xi)pv}{T}\right] - Ac_p(1+\xi)v$	—	$-\frac{\xi(1+\alpha)}{p\mu_2} \times [2ac^0_{p1} + (1-\alpha)c^0_{p2}]$
$\partial h$	$\frac{h\xi(1+\alpha)}{T}$	$\frac{\xi(1+\alpha)}{p}$	$-\frac{\xi(1+\alpha)(h-1)v}{pT}$	$\frac{\xi(1+\alpha)}{\mu_2 p T} [2ac^0_{p1} + (1-\alpha)c^0_{p2} - AR(1+\alpha)h]$	$\frac{\xi(1+\alpha)}{p\mu_2} \times [2ac^0_{p1} + (1-\alpha)c^0_{p2}]$	$\frac{\xi(1+\alpha)}{p\mu_2} \times [2ac^0_{p1} + (1-\alpha)c^0_{p2}]$	—

To find the value of  $\left(\frac{\partial x}{\partial y}\right)_z$  in Table 1, the expression in the row  $\partial x$  of the column  $z = \text{const}$  must be divided by the expression in the row  $\partial y$ . For example,  $\left(\frac{\partial i}{\partial s}\right)_p = c_p / \frac{c_p}{T} = T$ .

It should be emphasized that the condition  $\alpha = \text{const}$  is equivalent to the condition  $\mu = \text{const}$  since, according to another paper (Bibl.3),  $\mu = \frac{\mu_2}{1+\alpha}$  for a dissociating mixture. Moreover, it is possible to convert from the variable  $\alpha$  to the variable  $\mu$  by means of the relation  $d\mu = -\frac{\mu}{1+\alpha} d\alpha$ . Earlier (Bibl.3), we stated that a dissociating gas may be regarded as a model of an elementary

ideal associating gas. In the light of this reasoning, a complete set of easily calculated derivatives may be of interest to the further elaboration of the theory of associating gases, particularly when  $\mu = \text{const.}$

Certain derivatives in Table 1 represent the specific heats  $c_p$  and  $c_v$  of the dissociating mixture. The expressions for specific heat  $c_p$  and certain other derivatives are provided elsewhere [for example (Bibl.2, 4, 5)]. The specific heat in the presence of a constant pressure is

$$c_p = \frac{1}{\mu_2} [2ac_{p1} + (1-a)c_{p2} + AR(1+a)\xi h^2] \text{ kcal/kg/deg} \quad (2)$$

where (and henceforth)

$$\xi = \frac{a(1-a)}{2}, \quad h = \frac{\Delta I^\circ}{ART}.$$

The formula for  $c_v$  can be obtained by means of the relation

$$c_p - c_v = -T \left( \frac{\partial v}{\partial T} \right)_p^2 / \left( \frac{\partial v}{\partial p} \right)_T,$$

which implies (Table 1)

$$c_v = c_p - \frac{AR(1+a)(1+\xi \cdot h)^2}{\mu_2(1+\xi)} \text{ kcal/kg} \cdot \text{deg} \quad (3)$$

By means of this Table it is not difficult to derive the formulas for the coefficients of thermal expansion  $\alpha_T$  and isothermal and adiabatic compressibility  $\beta_T$  and  $\beta_A$ .

Below are presented formulas for a number of thermodynamic variables for a dissociating gas  $|X_2 \rightleftharpoons 2X|$  in the region of superheated and wet vapors, as well as along the saturation curve.

The differential Joule-Thomson effect  $\alpha_{J-T}$  in the superheated-vapor region

$$\alpha_{J-t} = \left( \frac{\partial T}{\partial p} \right)_t = \frac{\Delta I^0 (1 + \alpha) \xi}{p \mu_2 \cdot c_p} \quad (4)$$

If the corresponding quantities  $p$ ,  $\alpha$ ,  $c_p$ , are referred to the saturation curve, the resultant expression may be used to calculate the Joule-Thomson effect  $\alpha_{J-t}^{o-ph}$  on the saturation curve from the side of the one-phase region.

The quantity  $\alpha_{J-t}^{t-ph}$  in the wet-vapor region (and on the saturation curve from the side of the two-phase region) is determined from the Clapeyron-Clausius equation. Henceforth, it will be assumed that  $v' \ll v''$  on the saturation curve within the investigated region of parameters.

Then,

$$\alpha_{J-t}^{o-ph} = \frac{dT}{dp_{sat}} = \frac{ART^2 (1 + \alpha'')}{\mu_2 \cdot r \cdot p_{sat}} \quad (5)$$

where  $r$  is the specific heat of vaporization, calculated by the method described elsewhere (Bibl.3). The formula for the specific heat  $c_{sat}''$  for vapor on the saturation curve is

$$c_{sat}'' = \frac{di''}{dT} - \frac{r}{T} = \left( c_p'' - \frac{h \cdot \xi'' r}{T} - \frac{r}{T} \right) \text{ kcal/kg/deg} \quad (6)$$

Equation (3) can be used for calculating the specific heat  $c_{J-t}^{o-ph}$  on the saturation curve from the side of the one-phase region. To determine the specific heat  $c_{J-t}^{t-ph}$  on the saturation curve from the side of the two-phase region, eq.(6) by Sychev (Bibl.6) can be used.

This equation yields

$$c_{J-t}^{t-ph} = \frac{AR(1 + \alpha'')}{\mu_2} \frac{d \ln \sigma''}{dT} \left( \frac{1 + h\xi}{1 + \xi} - r_{hv} \right) \text{ kcal/kg/deg} \quad (7)$$

where

$$r_{hv} = \frac{r \mu_2}{ART (1 + \alpha'')}$$

In the analysis of flow processes, the speed of sound is an important parameter. If sound is identified with infinitesimal adiabatic perturbations propagating through a homogeneous (nonviscous, non-heat-conducting, etc.) /67 medium, it can be determined by the known formula

$$a = \sqrt{-gv' \left( \frac{\partial p}{\partial v} \right)_s} \quad (8)$$

Assuming that, during the propagation of a sound wave in a dissociating vapor, thermodynamic equilibrium may set in at any point and at any time instant, the expression  $\left( \frac{\partial p}{\partial v} \right)_s$  from Table 1 can be used for calculating the so-called "thermodynamic" or equilibrium speed of sound in superheated dissociating vapors that are saturated from the side of the one-phase region. Then,

$$a = \sqrt{g \cdot \frac{c_p}{c_v(1+\xi)} pv} \quad (9)$$

This last formula is a particular case of the equation derived elsewhere (Bibl.5) for calculating the speed of sound in a complex dissociating mixture of gases.

Practical calculations of the speed of sound often are based on the complex  $k_{son} = - \frac{v}{p} \left( \frac{\partial p}{\partial v} \right)_s$ , which we will term "sonic adiabatic exponent". It is obvious that

$$k_{son} = \frac{c_p}{c_v(1+\xi)} \quad (10)$$

for a dissociating gas.

The flow processes of wet vapors are one of the most complex fields of gas and hydrodynamics. Of special importance here are the problems of thermodynamic equilibrium (supercooling of vapors), homogeneity of the medium (formation of drops, their hydrodynamics in a sound wave, their surface energy). The diffi-

culty of solving the problem is aggravated by the effect of specific conditions, which sometimes is decisive and which is difficult to take into account, namely, the formation and removal of liquid films, the irregular moisture content of vapor over the channel cross section, etc.

Nevertheless, when analyzing the flow processes of wet vapor, the values of the speed of sound in some idealized flow may be of interest. To calculate the speed of sound in wet dissociating vapors, we assumed that:

- 1) the vapors are a homogeneous (from the hydrodynamic standpoint) reacting mixture of ideal gases ( $X_2 \approx 2X$ );
- 2) the degree of dryness  $x$  is sufficiently high; the volume and compressibility of the liquid phase can be neglected here;
- 3) Laplace's equation (8) is valid in calculating the speed of sound.

This makes it possible to calculate the speed of sound in a

Novikov (Bibl.7) under specific assumptions.

According to this method, we have, for wet vapor at  $x \gg 0$ ,

$$k_{son} = -\frac{v}{p} \left( \frac{\partial p}{\partial v} \right)_s = -\frac{r_{hv}}{T \left[ \frac{d \ln v''}{dT} - \frac{1}{r} \left( c''_{sat} - \frac{1-x}{x} c'_{sat} \right) \right]} \quad (11)$$

and the speed of sound,

$$a = \sqrt{\frac{g \cdot r \cdot x}{AT \left[ \frac{d \ln v''}{dT} - \frac{1}{r} \left( c''_{sat} - \frac{1-x}{x} c'_{sat} \right) \right]}} \quad (12)$$

For dissociating vapor on the saturation curve,  $c''_{sat}$  is determined from eq.(6); in addition, we obtain

$$\frac{d \ln v''}{dT} = \frac{1}{T} [1 - r_{hv} + \frac{r_{hv}}{T} (h - r_{hv})] \quad (13)$$



TABLE 2

$$\bullet c'_{\text{sat}} = 0.20080 - 0.75684 \cdot 10^{-4} + 0.75079 \cdot 10^{-6} \text{ (Bibl. 70)}$$

TABLE 3

$$a = V_g.$$

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TABLE 3 (cont'd)

0.4 kg/cm <sup>2</sup>											
0.5 kg/cm <sup>2</sup>											
$f_{sat} = 600; \mu'' = 624.6; r = 482.2; s'' = 0.778$											
$t, ^\circ\text{C}$	$\mu$	$\nu$	$l$	$s$	$c_p$	$c_v$	$\alpha$	$k_{son}$	$\mu$	$\nu$	$l$
700	0.9351	5.1042	628.92	0.79361	0.1910	0.1224	557.7	1.515	0.9298	4.8532	626.60
750	0.9377	5.4125	637.96	0.80271	0.1714	0.1060	573.9	1.552	0.9407	4.8058	636.17
800	0.9633	6.7116	646.17	0.81057	0.1584	0.0904	595.9	1.591	0.9547	4.5486	644.78
850	0.9774	6.0016	653.85	0.81760	0.1496	0.0771	614.3	1.633	0.9647	4.7649	653.75
900	0.9891	6.2877	661.16	0.82306	0.1438	0.0677	631.3	1.679	0.9720	4.9449	662.0
950	0.9981	6.5703	668.22	0.82987	0.1394	0.0604	648.4	1.730	0.9774	5.2446	670.3
1000	0.9997	6.8503	675.12	0.83536	0.1364	0.0550	663.8	1.787	0.9815	5.4703	676.2
1050	0.9997	7.1285	681.89	0.84056	0.1343	0.0511	678.4	1.851	0.9871	5.6940	682.0
1100	0.9998	7.4053	688.57	0.84554	0.1327	0.0480	692.4	1.921	0.9909	5.9166	687.9
1150	0.9998	7.6811	695.17	0.85030	0.1316	0.0452	705.9	1.996	0.9949	6.1382	693.8
1200	0.9998	7.9559	701.73	0.85482	0.1307	0.0426	719.6	2.075	0.9981	6.3588	700.1
1250	0.9998	8.2301	708.24	0.85913	0.1300	0.0402	731.6	2.158	0.9999	6.5768	707.0
1300	0.9998	8.5037	714.78	0.86331	0.1296	0.0379	743.9	2.245	0.9999	6.7901	713.80

1.0 kg/cm <sup>2</sup>											
$f_{sat} = 750; \mu'' = 630.1; r = 475.0; s'' = 0.759$											
$t, ^\circ\text{C}$	$\mu$	$\nu$	$l$	$s$	$c_p$	$c_v$	$\alpha$	$k_{son}$	$\mu$	$\nu$	$l$
750	0.9107	3.0122	632.76	0.77009	0.1971	0.1258	551.7	1.511	0.9150	2.2281	630.30
800	0.9382	3.2216	642.09	0.77903	0.1777	0.1118	565.4	1.572	0.9328	2.3536	647.54
850	0.9614	3.3619	650.60	0.78682	0.1642	0.1021	581.2	1.644	0.9462	2.4754	656.05
900	0.9808	3.5277	658.55	0.79373	0.1547	0.0903	604.2	1.720	0.9562	2.5912	664.04
950	0.9944	3.6933	666.09	0.80003	0.1479	0.0805	624.2	1.801	0.9640	2.7009	672.04
1000	0.9987	3.8581	673.35	0.80581	0.1430	0.0727	641.2	1.887	0.9700	2.8056	680.04
1050	0.9991	4.0229	680.42	0.81126	0.1394	0.0660	657.2	1.978	0.9748	2.9053	688.04
1100	0.9992	4.1875	687.32	0.81641	0.1368	0.0602	673.2	2.072	0.9786	3.0000	696.04
1150	0.9993	4.3521	694.11	0.82154	0.1348	0.0550	689.2	2.168	0.9816	3.0907	704.04
1200	0.9994	4.5167	700.81	0.82654	0.1333	0.0502	705.2	2.265	0.9840	3.1763	712.04
1250	0.9994	4.6813	707.45	0.83152	0.1322	0.0456	721.2	2.362	0.9860	3.2572	720.04
1300	0.9994	4.8459	714.04	0.83647	0.1313	0.0412	737.2	2.460	0.9875	3.3333	728.04

1.5 kg/cm <sup>2</sup>											
$f_{sat} = 905; \mu'' = 633.8; r = 470.0; s'' = 0.734$											
$t, ^\circ\text{C}$	$\mu$	$\nu$	$l$	$s$	$c_p$	$c_v$	$\alpha$	$k_{son}$	$\mu$	$\nu$	$l$
850	0.9040	1.5457	642.83	0.74254	0.1953	0.1230	598.1	1.521	0.8777	1.1432	638.53
900	0.9223	1.6300	652.15	0.75067	0.1793	0.1118	609.3	1.568	0.8902	1.2718	648.53
950	0.9364	1.7120	660.79	0.75788	0.1674	0.1035	620.3	1.616	0.9016	1.3931	658.53
1000	0.9474	1.7920	669.34	0.76433	0.1585	0.0973	631.4	1.665	0.9125	1.5053	668.53
1050	0.9560	1.8708	677.88	0.77003	0.1516	0.0926	642.5	1.715	0.9216	1.6109	678.53
1100	0.9629	1.9482	686.42	0.77503	0.1467	0.0891	653.6	1.767	0.9294	1.7109	688.53
1150	0.9684	2.0247	694.96	0.77953	0.1428	0.0865	664.7	1.820	0.9361	1.8059	698.53
1200	0.9727	2.0995	703.50	0.78359	0.1399	0.0845	675.8	1.873	0.9419	1.8964	708.53
1250	0.9763	2.1727	712.04	0.78706	0.1376	0.0830	686.9	1.926	0.9468	1.9814	718.53
1300	0.9793	2.2450	720.58	0.79006	0.1358	0.0816	698.0	1.979	0.9508	2.0614	728.53

TABLE 3 (cont'd)

t, °C	3 kg/cm <sup>2</sup>										4 kg/cm <sup>2</sup>									
	$t_{sat} = 80.4; \nu' = 640.6; r = 460.1; s'' = 0.708$										$t_{sat} = 83.6; \nu' = 644.1; r = 465.2; s'' = 0.707$									
	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$
900	0.8400	0.7887	642.01	0.70868	0.2119	0.1331	599.4	1.502	0.8530	0.6143	647.11	0.69938	0.2084	0.1300	603.9	1.509	0.8530	0.6143	647.11	0.69938
950	0.8336	0.8326	652.13	0.71713	0.1949	0.1214	611.7	1.527	0.8755	0.6472	657.10	0.70730	0.1983	0.1197	623.6	1.532	0.8755	0.6472	657.10	0.70730
1000	0.8273	0.8752	661.61	0.72464	0.1814	0.1122	631.7	1.559	0.8939	0.6792	666.48	0.71458	0.1811	0.1114	648.0	1.552	0.8939	0.6792	666.48	0.71458
1050	0.8213	0.9168	670.31	0.73140	0.1709	0.1040	650.5	1.560	0.9091	0.7106	675.30	0.72115	0.1778	0.1048	661.4	1.570	0.9091	0.7106	675.30	0.72115
1100	0.8155	0.9575	678.95	0.73761	0.1625	0.0992	668.3	1.585	0.9216	0.7412	683.69	0.72718	0.1634	0.0995	678.8	1.585	0.9216	0.7412	683.69	0.72718
1150	0.8100	0.9975	688.24	0.74335	0.1559	0.0948	685.1	1.599	0.9318	0.7714	691.71	0.73271	0.1571	0.0953	693.2	1.608	0.9318	0.7714	691.71	0.73271
1200	0.8042	1.0389	698.31	0.74890	0.1508	0.0914	700.9	1.610	0.9402	0.8010	699.45	0.73785	0.1521	0.0920	710.8	1.608	0.9402	0.8010	699.45	0.73785
1250	0.8000	1.0767	708.76	0.75359	0.1467	0.0887	715.8	1.619	0.9472	0.8303	706.94	0.74268	0.1482	0.0894	725.6	1.617	0.9472	0.8303	706.94	0.74268
1300	0.8000	1.1141	708.96	0.75826	0.1435	0.0866	730.1	1.626												

t, °C	5 kg/cm <sup>2</sup>										6 kg/cm <sup>2</sup>									
	$t_{sat} = 97.0; \nu' = 647.0; r = 451.4; s'' = 0.689$										$t_{sat} = 100.0; \nu' = 649.4; r = 447.8; s'' = 0.682$									
	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$
1000	0.8510	0.5110	653.11	0.69368	0.2061	0.1230	616.8	1.517	0.8285	0.4207	649.41	0.68225	0.2118	0.1319	610.5	1.591	0.8285	0.4207	649.41	0.68225
1050	0.8723	0.5372	662.92	0.70123	0.1898	0.1169	636.5	1.534	0.8522	0.4428	659.52	0.69011	0.1973	0.1286	630.7	1.627	0.8522	0.4428	659.52	0.69011
1100	0.8900	0.5627	672.16	0.70808	0.1769	0.1096	655.4	1.557	0.8721	0.4645	669.21	0.69724	0.1858	0.1258	649.0	1.646	0.8721	0.4645	669.21	0.69724
1150	0.9047	0.5878	680.91	0.71438	0.1700	0.1037	673.3	1.573	0.8888	0.4857	682.28	0.70375	0.1758	0.1234	668.3	1.663	0.8888	0.4857	682.28	0.70375
1200	0.9168	0.6123	689.23	0.72013	0.1628	0.0980	696.2	1.587	0.9026	0.5065	695.13	0.70969	0.1680	0.1207	685.5	1.677	0.9026	0.5065	695.13	0.70969
1250	0.9283	0.6364	697.24	0.72544	0.1571	0.0951	706.2	1.598	0.9141	0.5268	703.06	0.71517	0.1648	0.1183	701.8	1.690	0.9141	0.5268	703.06	0.71517
1300	0.9352	0.6601	704.96	0.73042	0.1524	0.0920	721.4	1.608	0.9237	0.5468	703.06	0.72028	0.1668	0.1161	717.4		0.9237	0.5468	703.06	0.72028

t, °C	7 kg/cm <sup>2</sup>										8 kg/cm <sup>2</sup>									
	$t_{sat} = 102.6; \nu' = 651.6; r = 444.9; s'' = 0.677$										$t_{sat} = 106.0; \nu' = 653.7; r = 442.0; s'' = 0.673$									
	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$
1050	0.8334	0.3757	656.51	0.69054	0.2037	0.1255	625.5	1.517	0.8393	0.3423	663.81	0.67974	0.1965	0.1205	640.2	1.628	0.8393	0.3423	663.81	0.67974
1100	0.8552	0.4046	666.43	0.69792	0.1914	0.1173	645.1	1.536	0.8592	0.3686	673.40	0.68663	0.1859	0.1134	659.4	1.645	0.8592	0.3686	673.40	0.68663
1150	0.8736	0.4330	675.78	0.70453	0.1812	0.1105	661.4	1.554	0.8760	0.3745	682.49	0.69200	0.1769	0.1075	677.3	1.661	0.8760	0.3745	682.49	0.69200
1200	0.8890	0.4310	684.94	0.70974	0.1727	0.1049	681.4	1.569	0.8901	0.3901	691.16	0.69860	0.1695	0.1027	694.3	1.674	0.8901	0.3901	691.16	0.69860
1250	0.9018	0.4487	693.11	0.70837	0.1657	0.1004	697.9	1.581	0.9019	0.4055	699.45	0.70401	0.1634	0.0987	710.3	1.680	0.9019	0.4055	699.45	0.70401
1300	0.9126	0.4660	701.22	0.71160	0.1600	0.0958	713.6	1.593												

t, °C	9 kg/cm <sup>2</sup>										10 kg/cm <sup>2</sup>									
	$t_{sat} = 107.3; \nu' = 655.6; r = 439.4; s'' = 0.668$										$t_{sat} = 109.2; \nu' = 657.4; r = 437.1; s'' = 0.665$									
	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$	$\alpha$	$\nu$	$l$	$s$	$c_p$	$c_p$	$\alpha$	$k_{son}$	$\alpha$	$k_{son}$
1100	0.8242	0.3017	661.32	0.67246	0.2011	0.1233	636.5	1.621	0.8709	0.2694	659.97	0.66588	0.2051	0.1234	632.5	1.611	0.8709	0.2694	659.97	0.66588
1150	0.8455	0.3164	671.14	0.67950	0.1901	0.1160	655.4	1.638	0.8824	0.2827	668.99	0.67396	0.1943	0.1181	651.7	1.630	0.8824	0.2827	668.99	0.67396
1200	0.8636	0.3307	680.44	0.68591	0.1808	0.1098	673.5	1.654	0.8915	0.2957	678.46	0.67960	0.1843	0.1120	667.9	1.644	0.8915	0.2957	678.46	0.67960
1250	0.8787	0.3447	689.29	0.69179	0.1720	0.1048	690.6	1.668	0.8978	0.3084	687.48	0.68460	0.1763	0.1067	687.3	1.652	0.8978	0.3084	687.48	0.68460
1300	0.8916	0.3585	697.75	0.69725	0.1666	0.1006	706.9	1.680	0.9016	0.3209	696.00	0.69115	0.1705	0.1023	700.8	1.671	0.9016	0.3209	696.00	0.69115

TABLE 3 (cont'd)

t, °C	12 kg/cm <sup>2</sup>										14 kg/cm <sup>2</sup>									
	t <sub>sat</sub> = 1129; t'' = 660.7; r = 432.7; s'' = 0.659										t <sub>sat</sub> = 1162; t'' = 663.8; r = 428.7; s'' = 0.631									
	a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>			a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>		
150	0.8079	0.2325	664.95	0.66180	0.2004	0.1223	644.9	1.521			0.8062	0.2063	671.32	0.65911	0.1936	0.1189	657.6	1.527		
1200	0.8220	0.2434	674.75	0.66856	0.1975	0.1158	663.5	1.537			0.8279	0.2156	683.69	0.66547	0.1868	0.1131	675.5	1.542		
1250	0.8171	0.2542	684.07	0.67475	0.1820	0.1102	681.2	1.551			0.8447	0.2247	690.93	0.67135	0.1793	0.1082	692.0	1.555		
1300	0.8025	0.2647	692.95	0.68048	0.1747	0.1055	687.9	1.564												

t, °C	16 kg/cm <sup>2</sup>										18 kg/cm <sup>2</sup>									
	t <sub>sat</sub> = 1192; t'' = 666.6; r = 425.0; s'' = 0.680										t <sub>sat</sub> = 1219; t'' = 669.1; r = 421.7; s'' = 0.646									
	a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>			a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>		
1200	0.788	0.1766	668.14	0.65965	0.1999	0.1215	652.3	1.519			0.7930	0.1945	675.13	0.65013	0.1946	0.1178	665.7	1.536		
1250	0.809	0.1868	677.92	0.65735	0.1910	0.1166	670.4	1.533			0.8121	0.1717	684.62	0.65626	0.1867	0.1127	683.1	1.539		
1300	0.827	0.1949	687.23	0.66336	0.1832	0.1108	687.7	1.547												

t, °C	20 kg/cm <sup>2</sup>										22 kg/cm <sup>2</sup>									
	t <sub>sat</sub> = 1245; t'' = 671.6; r = 418.4; s'' = 0.704										t <sub>sat</sub> = 1269; t'' = 673.8; r = 415.2; s'' = 0.640									
	a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>			a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>		
1250	0.7771	0.1467	672.51	0.64384	0.1976	0.1197	661.3	1.519			0.7831	0.1382	679.81	0.64404	0.1924	0.1161	674.8	1.527		
1300	0.7972	0.1533	682.14	0.64986	0.1897	0.1148	671.8	1.533												

t, °C	24 kg/cm <sup>2</sup>										26 kg/cm <sup>2</sup>									
	t <sub>sat</sub> = 1292; t'' = 676.1; r = 412.1; s'' = 0.608										t <sub>sat</sub> = 1316; t'' = 678.3; r = 408.9; s'' = 0.574									
	a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>			a	v	l	s	c <sub>p</sub>	c <sub>g</sub>	a	k <sub>son</sub>		
1200	0.7606	0.1258	677.59	0.63671	0.1947	0.1175	671.0	1.531												

The relations derived above were used in calculating the corresponding thermodynamic properties of potassium vapors at 500 - 1300°C for which we had previously (Bibl.3) calculated, in the same range of parameters, the saturation pressures, degrees of dissociation, specific volumes, enthalpies, entropies, and heats of vaporization. In addition, the calculation methods were verified, as was the validity of the basic assumptions. The vapors of potassium were regarded as an equilibrium mixture of dissociating ( $K_2 \rightleftharpoons 2K$ ) monatomic and diatomic ideal gases. The basic source data were taken from Evans (Bibl.8, 9). We assumed a heat of dissociation  $D_0^\circ(K_2) = 11,842 + 1,000$  kcal/mole. The saturated vapor pressure was calculated from the conditions of vapor-liquid equilibrium on the basis of experimental findings (Bibl.10) on the enthalpy of liquid potassium, which were extrapolated from 800 to 1300°C.

Table 2 presents the following thermodynamic properties of saturated potassium vapors: specific heat  $c_{p,t}''$ ,  $c_{p,0}''$ ,  $c_{p,0}''$ , and  $c_{p,t}''$ ; differential Joule-Thomson effect  $\alpha_{j,0}''$  and  $\alpha_{j,t}''$ , sonic adiabatic exponent  $k_{s,0}''$  and  $k_{s,t}''$ , and speeds of sound  $a_{0}''$  and  $a_{t}''$ .

The thermodynamic properties of superheated potassium vapors, calculated in this investigation and earlier (Bibl.3), are presented in Table 3. These properties are: degree of dissociation  $\alpha$ , specific volume  $v$  in  $m^3/kg$ ; enthalpy  $i$  in kcal/kg and entropy  $s$  in kcal/kg $^\circ K$ , the last two being calculated by taking the state of the condensed phase at  $t = 0^\circ C$  and  $p = 1$  atm as the computational basis; specific heats  $c_p$  and  $c_v$  in kcal/kg $^\circ$ ; sonic adiabatic exponent  $k_{s,0} = - \frac{v}{p} \left( \frac{\partial p}{\partial v} \right)_s$ , and, lastly, speed of sound  $a$  in m/sec.

The number of digits in the Tables correspond to the smoothness of the functions, which fundamentally equals  $\pm 1$  of the last significant figure. The kilocalories in this investigation were calculated according to the GOST State

Standard 8550-61. The acceleration due to gravity was taken as normal:  $g = 9.80665 \text{ m/sec}^2$ .

The results of the calculations on the superheated-vapor side are represented by the  $c_p, t$ -chart (Fig.1), the  $k_{s,0}, t$ -chart (Fig.2) and by the  $a, s$ -chart (speed of sound - entropy) (Fig.3), where the latter includes the region of wet vapor up to degree of dryness of  $x \geq 0.6$ . /68

An analysis of the findings warrants the following statements:

1. The specific heat  $c_p$  of dissociating gases is largely a function of pressure; this is evident from eqs.(2) and (3) and Fig.1; moreover, eq.(2) implies that the isotherms have maxima, cut off by the saturation curve (Fig.1). Owing to the heat of dissociation, the total  $c_p$  is considerably higher than the so-called "frozen" specific heat described by the first two terms of eq.(2). /70

The curve of the specific heat  $c_p$  on the saturation line has an unusual maximum for dissociating ideal potassium vapors. Our earlier calculations (Bibl.3) show that this maximum either gets smoothed out or disappears under real conditions.

The total error in calculating  $c_p$ , due to the inaccuracy of source data and particularly due to the error in determining the heat of dissociation, as well as due to neglecting the real conditions of vapor components at  $24 \text{ kg/cm}^2$  and  $1300^\circ \text{C}$ , does not exceed 15%.

The  $c_v, t$ -chart in the region of the studied parameters resembles the  $c_p, t$ -chart (Fig.1).

2. Like certain other thermodynamic functions, the speed of sound and the "sonic" adiabatic exponent of dissociating gases are largely a function not only of temperature but also of pressure. A similar relationship should occur, e.g. for water vapor, if allowance is made for the above-mentioned similarity be-

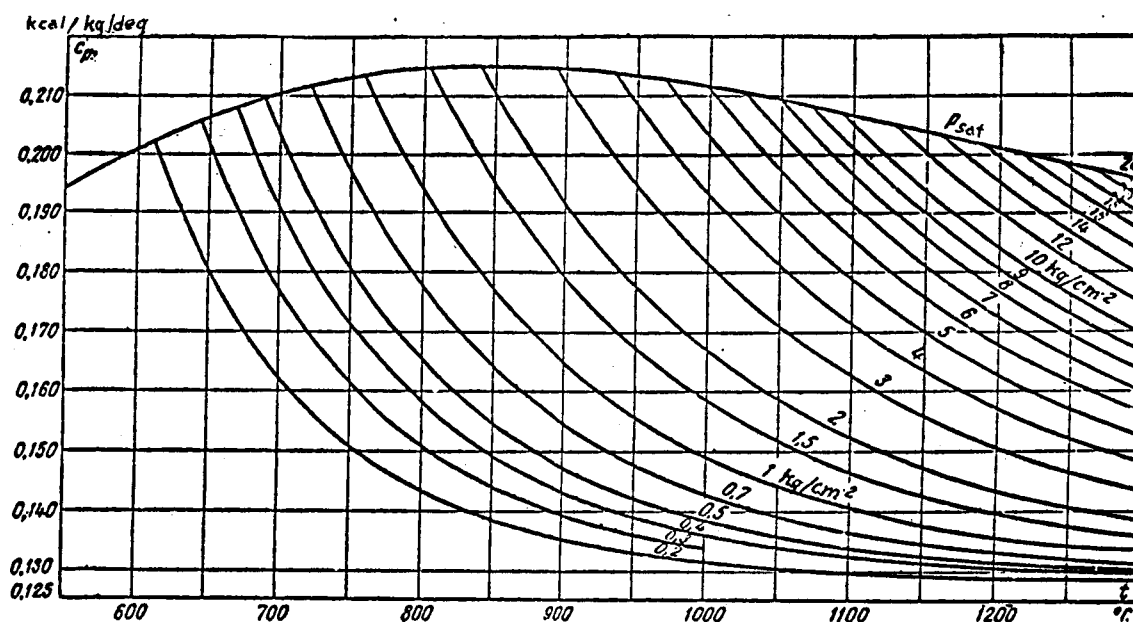


Fig.1 Specific Heat  $c_p$  of Dissociating Potassium Vapors Ordinate: kcal/kg/°

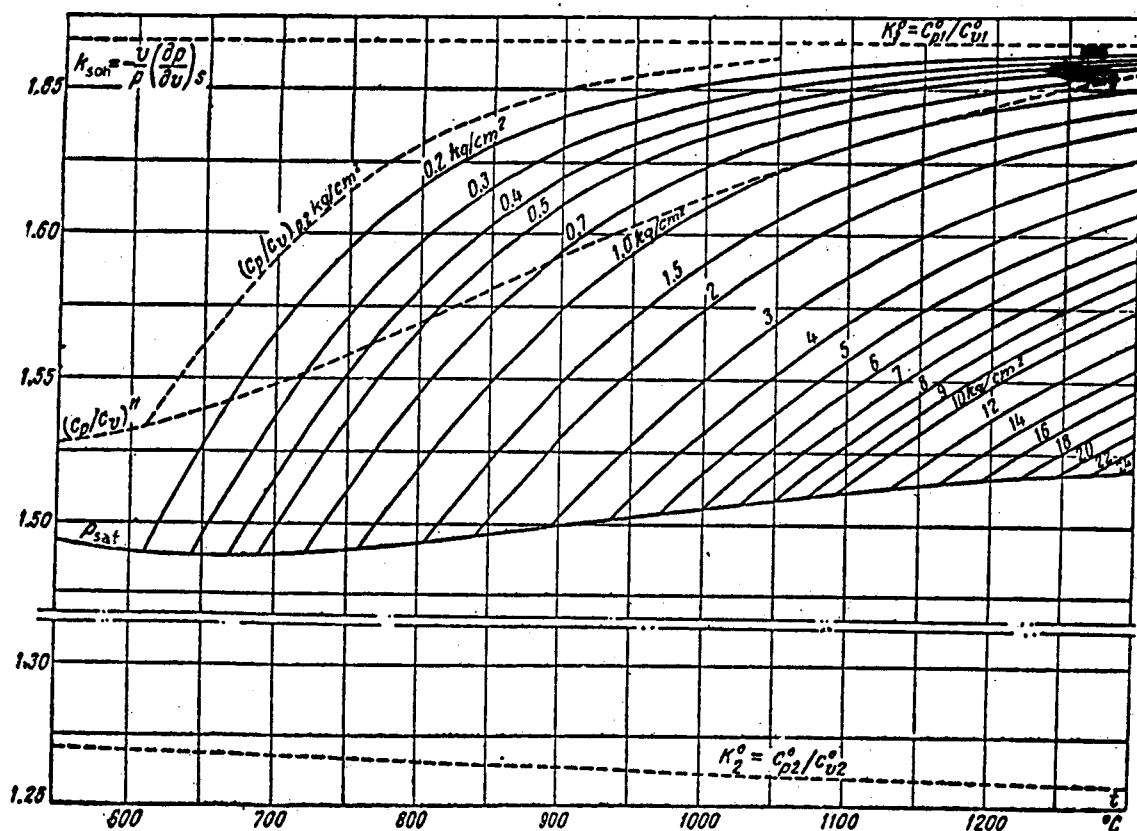


Fig.2 Sonic Adiabatic Exponent of Dissociating Potassium Vapors

tween the associating (in the sense of Van Der Waals) and dissociating gases.

The  $k_{s.o.n}$  differs markedly from the ratio of the specific heats  $c_p/c_v$  [see eq.(10) and Fig.2] and only tends to the latter along the isobars at a rise in temperature, i.e., when the degree of dissociation  $\alpha \rightarrow 1$ .

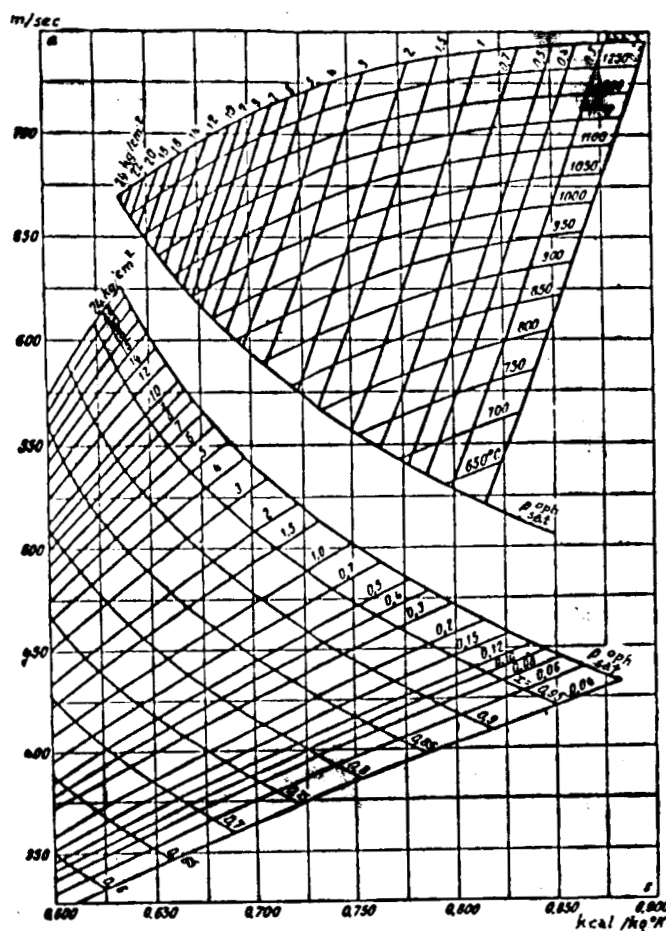


Fig.3 Speed of Sound - Entropy Chart for Potassium Vapors

It should be emphasized that this "sonic" adiabatic exponent  $k_{s.o.n}$  generally differs from the exponent  $k$ , which is determined by the thermal equation of the adiabatic line  $p v^k = \text{const.}$

In fact, the exponent  $k$ , just as  $k_{s.o.n}$ , is generally a variable quantity. Following the logarithmic conversion of the adiabatic line and subsequent differentiation with respect to  $v$  for  $s = \text{const}$ , we obtain the connectivity equa-



tion

$$k_{son} = \frac{k}{1 + p \frac{1}{\rho} \left( \frac{\partial k}{\partial p} \right)}. \quad (14)$$

Obviously, the mentioned divergence between the adiabatic exponents ( $k_{son}$  and  $k$ ) complicates the calculation of flow processes from the most elementary form of the Bernoulli equation.

In this connection, when calculating the critical flow regimes of the dissociating vapors of potassium, it is expedient to determine the rate of flow according to the corresponding values of the heat drop in the  $i, s$ -diagram (Bibl.3) and compare them with the speed of sound as given in the tables or in the  $a, s$ -diagram (Fig.3).

3. In wet vapor, the "sonic" adiabatic exponent  $k_{son}$  is relatively [eq.(11)] independent of the degree of dryness and may, in first approximation, be assumed equal to  $k_{s,0n}^{tp,h}$  on the isobars (or isotherms).

It should be emphasized that, by contrast with the speed of sound, the exponent  $k_{s,0n}^{tp,h}$  is not conceptually related to the restriction on the hydrodynamic homogeneity of the medium.

On the whole, however, the calculation of the speed of sound in dissociating vapors in general, and in dissociating wet vapors in particular, is only of an approximate nature considering that the problems of thermodynamic equilibrium during variations in parameters and during passage of sound waves require further more detailed investigations.

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